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From Brayton-Moser formulation to Port Hamiltonian representation: the CSTR case study

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Abstract: This paper shows that any thermodynamic variable fulfilling some stability criterion can be used as Hamiltonian for pseudo hamiltonian representation of a non isothermal Continuous Stirred Tank Reactor (CSTR) model. More precisely it is shown that from Brayton-Moser formulation is obtained some port hamiltonian representation with negative dissipation. This result is shown for reaction $A \rightleftharpoons B$.

Keywords: Irreversible thermodynamics, CSTR, Port Hamiltonian systems, Brayton-Moser formulation, passivity.

1. INTRODUCTION

This paper deals with modeling of continuous single phase chemical reactors in Port Hamiltonian framework using irreversible thermodynamics. More precisely, the Port (pseudo) Hamiltonian modeling will be obtained by using Brayton-Moser formulation (B-M formulation) based on a structured representation of the system with the variables directly issued from thermodynamic framework. It shows that there exists some general thermodynamic criterion (including the irreversible entropy production due to chemical reaction) permitting to determine the (strictly) negative definite matrix Q for the B-M formulation. In other words, any thermodynamic variable verifying this criteria is usable as an Hamiltonian function. This port hamiltonian representation will be used for control design of the CSTRs thanks to IDA-PBC approach Ortega (2002); Favache (2009); Ramírez (2009); Dörfler (2009) using the thermodynamic availability function (Ydstie and Alonso (1997); Ruszkowski (2005)) as desired closed loop hamiltonian. Although, it is generally difficult to solve the so called matching PDE equation to find the state feedback able to assign the desired closed loop Hamiltonian, it has been shown in Hoang (2010a,b) that this matching equation can be easily solved with this previous choice.

Let us note that in contrast with mechanical and electrical systems where connections between energy and control are today fairly well understood (van der Schaft (2000a); Maschke (2000)), links between physics and process control in a Port Hamiltonian based view are quite difficult to exhibit from geometrical point of view (Eberard (2007)) and need considerable attentions. In fact, the chemical reactor models, and in particular the reference case study known as the Continuous Stirred Tank Reactor (CSTR), belong to nonlinear non-equilibrium thermodynamic sys-

tems because of reaction kinetics and irreversibilities of the coupling between matter and temperature. Following the first principle of Thermodynamics, the total energy (the energy of the simple system under consideration and its surrounding medium) is conserved. Yet, this energy changes of nature moving irreversibly from the material domain to the thermal domain. As a matter of fact the internal energy cannot be considered as an Hamiltonian function because it does not allow to express the inherent irreversibility of the system governed by the Second Law of Thermodynamics. The variation of the internal energy is only to change molecular arrangements and chemical structure of species. As a consequence, the links between thermodynamics and system theory have to be characterized more precisely in order to exhibit thermodynamic variables usable both for Port Hamiltonian based modeling and control design.

This subject has attracted some interest in the literature (Hangos *et al.* (2001); Eberard (2007); Otero-Muras (2008); Dörfler (2009); Favache (2009); Hudon (2008); Ramírez (2009); Hoang (2010a,b)) due to the fact that the Port Hamiltonian based methodology has been met with some success in the field of chemical engineering. Even if such formulation does not formally exist (Eberard (2007)), a pseudo Hamiltonian formulation allows us to find appropriate stabilization laws using the passivity based control e.g. for simple chemical reactors (Bao and Lee (2007); Favache (2009); Ramírez (2009)).

Let us analyze some obtained results for Port Hamiltonian modeling of CSTRs as proposed in (Otero-Muras (2008); Ramírez (2009); Dörfler (2009); Favache (2010)). In the case of (Ramírez (2009)), dissipation term does not capture the inherently irreversible nature of the CSTR and the Hamiltonian is not linked to any thermodynamic

variable. The same situation is given in (Dörfler (2009)). The use of the physical variable for the Hamiltonian is done in (Otero-Muras (2008)), where the authors propose an Hamiltonian representation of closed reaction networks in the isothermal case. In their case the local Hamiltonian is not the Gibbs free energy (as in Hoang (2010b)) but it is locally linked to the chemical affinity. Using the irreversible entropy production (due to chemical reaction) as Hamiltonian potential is given in Favache (2010) with some restrictions on the reaction kinetics. However, its dissipation term is not obvious. In our recent works (Hoang (2010a,b)), a thermodynamically consistent Hamiltonian pseudo representation of the CSTRs model using the thermodynamic potentials (Gibbs free energy G and opposite of entropy $-S$ for isothermal and non-isothermal cases respectively) as Hamiltonian function is given. The dissipation term is then expressed by the irreversible entropy production due to chemical reaction.

This paper first shows that, a pseudo PH representation for continuous stirred tank reactor (CSTR) can be also obtained from the B-M formulation by using thermodynamic variables. The paper generalizes the results of (Otero-Muras (2008); Hoang (2010a,b)). This formulation is based on a structured representation of systems with the variables directly coming from thermodynamic considerations. In this paper, we show that the following candidate variables can be chosen as hamiltonian function:

- The opposite of entropy $-S$ (extensive variable).
- The chemical affinity \mathcal{A} (intensive variable).

As a consequence, the dissipation term is also linked to the natural irreversibility due to chemical reaction.

This paper is organized as follows: in section 2, an overview on the links between the B-M formulation and Port controlled Hamiltonian representation is given. In section 3 a CSTR case study with one reaction $\nu_A A = \nu_B B$ is presented and analyzed from a thermodynamics based point of view. The *Thermodynamic Availability* concept is recalled. In the section 4, we present a stability criteria for thermodynamic variables and the decomposition of the availability into the thermal and material parts for CSTRs. This stability criteria is then used to find the solution of the B-M formulation for a CSTR with one reaction scheme $\nu_A A = \nu_B B$ in Section 5. As a consequence, the thermodynamically consistent Port Hamiltonian modeling is easily obtained.

2. PORT CONTROLLED HAMILTONIAN REPRESENTATION AND B-M FORMULATION

Here we are interested in open chemical systems whose mathematical modeling is affine with respect to control input u and is given by the following set of ODE's :

$$\frac{dx}{dt} = f(x) + g(x) u \quad (1)$$

where $x = x(t) \in \mathbb{R}^n$ is the state vector, $f(x) \in \mathbb{R}^n$ represents the smooth nonlinear function with respect to x , $g(x) \in \mathbb{R}^{n \times m}$ is the input-state map and $u \in \mathbb{R}^m$ is the input.

2.1 B-M formulation

B-M formulation (Brayton and Moser (1964)) leads

- (1) to find a matrix $Q(x) : \mathbb{R}^n \rightarrow \mathbb{R}^{n \times n}$ that satisfies the two following conditions:

- (C1) It is non singular (or invertible)
- (C2) Its symmetry part is negative definite:

$$Q(x) + Q(x)^t \leq 0 \quad (2)$$

where the exponent t holds for the matrix transpose.

- (2) to write the system dynamics (1) into the following equivalent form :

$$Q(x) \frac{dx}{dt} = \nabla_x P(x) + G(x)u \quad (3)$$

with $P(x) : \mathbb{R}^n \rightarrow \mathbb{R}$ is smooth potential function with respect to x . ∇_x represents the Gradient operator in x .

By identifying (1) et (3), we obtain the following relations:

$$\nabla_x P(x) = Q(x)f(x) \quad (4)$$

and

$$G(x) = Q(x)g(x) \quad (5)$$

The sufficient and necessary conditions for the existence of (3) is the symmetry of the Hessian matrix $\mathbb{H}(P)$ of $P(x)$:

$$\mathbb{H}(P) = \left(\mathbb{H}(P) \right)^t \quad (6)$$

Remark 1. The B-M formulation requires some possibly heavily mathematical calculations in general (solutions for Partial Differential Equation (PDE)). We leave the reader to refer to (Favache (2009, 2010)) for the different applications of the B-M formulation to modeling of CSTRs.

2.2 Links with the Port controlled Hamiltonian formulation (PCH)

Because Q is invertible, the B-M form (3) can be written in the equivalent one:

$$\frac{dx}{dt} = Q(x)^{-1} \nabla_x P(x) + g(x)u \quad (7)$$

As we know, any square matrix can be split into two parts: symmetric part and skew-symmetric part. Eq. (7) is then transformed into the following form:

$$\frac{dx}{dt} = \left[\frac{Q(x)^{-1} - Q(x)^{-1t}}{2} + \frac{Q(x)^{-1} + Q(x)^{-1t}}{2} \right] \nabla_x P(x) + g(x)u \quad (8)$$

The dynamical equation (8) can be identified to a general class of the so called Port controlled Hamiltonian systems with dissipation given by (Maschke (2000); Brogliato (2007); van der Schaft (2000a,b)):

$$\begin{cases} \frac{dx}{dt} = [J(x) - R(x)] \nabla_x \mathcal{H}(x) + g(x)u \\ y = g(x)^t \nabla_x \mathcal{H}(x) \end{cases} \quad (9)$$

where:

$$\begin{cases} \mathcal{H}(x) = P(x) \\ J(x) = \frac{Q(x)^{-1} - Q(x)^{-1t}}{2} \\ R(x) = -\frac{Q(x)^{-1} + Q(x)^{-1t}}{2} \end{cases} \quad (10)$$

the smooth function $\mathcal{H}(x) = P(x) : \mathbb{R}^n \rightarrow \mathbb{R}$ represents the Hamiltonian storage function (or the energy); $J(x) = -J(x)^t$ and $R(x) = R(x)^t \geq 0$ are the structure matrices and correspond to the natural interconnection matrix and the damping matrix, respectively; $u, y \in \mathbb{R}^m$ are the control input and the output, respectively, and are power conjugated port variables.

The energy balance immediately follows from (9):

$$\frac{d\mathcal{H}(x)}{dt} = - \left[\frac{\partial \mathcal{H}(x)}{\partial x} \right]^t R(x) \left[\frac{\partial \mathcal{H}(x)}{\partial x} \right] + u^t y \quad (11)$$

The system (9) is passive in the sense that the dissipation

$$d = - \left[\frac{\partial \mathcal{H}(x)}{\partial x} \right]^t R(x) \left[\frac{\partial \mathcal{H}(x)}{\partial x} \right] < 0 \quad (12)$$

is always negative and the Hamiltonian $\mathcal{H}(x)$ is bounded from below (van der Schaft (2000b); Brogliato (2007)). The term d defined by (12) corresponds to natural dissipation (energy lost due to friction/damping in a mechanical systems or due to resistance in *RLC* electrical system (van der Schaft (2000a); Maschke (2000)) for example). The following inequality immediately follows from (11) and (12)

$$\overbrace{\mathcal{H}(x(t_2)) - \mathcal{H}(x(t_1))}^{\text{energy storage}} \leq \overbrace{\int_{t_1}^{t_2} u(\tau)^t y(\tau) d\tau}^{\text{energy supply}} \quad (13)$$

In this case (13) shows that a passive system cannot store more energy than the one supplied to it from the environment due to the dissipated energy. In other words, we can only extract a finite amount of energy from a passive system. From here, a feedback law of the form $u = -Ky$ with $K > 0$ for instance, returns this system to be dissipative.

Remark 2. Port Hamiltonian formulation is related to the existence of a geometric interconnection structure named the Dirac structure. This linear structure implies that J, R may depend only on x and the matrix R necessarily verifies the strictly positive definite condition, $\forall e \neq 0 : e^t R(x) e \geq 0$. Unfortunately but it is not necessarily the case for chemical reaction systems (see Hoang (2010a,b)) due to strong non linearity appearing in thermodynamic and constitutive relations (reaction kinetics for instance). In that situation, it is called Port pseudo Hamiltonian formulation.

3. CSTR CASE STUDY

3.1 Classical model of CSTR

Let us consider a jacketed reactor with one reaction involving 2 chemical species A and B :

$$\nu_A A = \nu_B B \quad (14)$$

Let us assume that the reactor is modelled with the so called CSTR model which assumes uniform properties such as temperature, pressure or concentrations inside the reactor. As a consequence, the reaction mixture is homogeneous.

Remark 3. The reaction under consideration can be either an equilibrated reaction (in this case, " $=$ " is replaced by " \rightleftharpoons ") or a non equilibrated reaction (in this case, " $=$ " is replaced by " \rightarrow ").

In the case the reaction (14) is an equilibrated reaction, A is not only the reactant (with respect to the forward reaction) but also the product (with respect to the reverse reaction). The same situation also holds for B . As a consequence for the dynamic representation, ν_A and ν_B are the suitable signed stoichiometric coefficients with the following convention :

$$\begin{cases} \nu_A < 0 & \text{since } A \text{ appears on the left side of (14)} \\ \nu_B > 0 & \text{since } B \text{ appears on the right side of (14)} \end{cases} \quad (15)$$

Remark 4. the net reaction rate r is equal to :

$$r = (r_f - r_r) \quad (16)$$

where r_f and r_r are the forward and reserve reaction rates respectively.

Let us consider the following hypotheses:

- (H1) The fluid mixture is ideal, incompressible and under isobaric conditions.
- (H2) In the inlet, the reactor is fed by the species A and B at a fixed temperature T_I .
- (H3) The heat flow coming from the jacket \dot{Q}_J ,

$$\dot{Q}_J = \lambda(T_J - T) \quad (17)$$

with λ heat exchange coefficient and inlet molar flow rates (F_{AI}, F_{BI}) are used as inputs.

3.2 Thermodynamics based view for CSTR modeling

In a thermodynamics based view, the system variables are divided into extensive variables such as the internal energy U , the entropy S , the volume V , the molar number N_i and into intensive variables as the temperature T , the pressure P , the chemical potential μ_i . The variation of the internal energy U (with isobaric conditions the pressure p is constant, we use the enthalpy H instead of the internal energy U) can be derived from the variation of the extensive variables using the Gibbs equation:

$$dH = \sum_{i=A}^B \mu_i dN_i + T dS \quad (18)$$

Since the energy H is an extensive variable, it is a homogenous function of degree 1 of (N_A, N_B, S) (Callen (1985)). From Euler's theorem we get:

$$H(N_A, N_B, S) = \sum_{i=A}^B \mu_i N_i + TS \quad (19)$$

As a consequence of eq. (18):

$$dS = \sum_{i=A}^B \frac{-\mu_i}{T} dN_i + \frac{1}{T} dH \quad (20)$$

Since the entropy S is also an extensive variable, we get:

$$S(N_A, N_B, H) = \sum_{i=A}^B \frac{-\mu_i}{T} N_i + \frac{1}{T} H \quad (21)$$

(20) can be written in a compact form as:

$$dS = w^t dZ \quad \Rightarrow \quad w(Z)^t = \frac{\partial S(Z)}{\partial Z} \quad (22)$$

with

$$w(Z) = \left(\frac{-\mu_A}{T}, \frac{-\mu_B}{T}, \frac{1}{T} \right)^t, \quad Z = (N_A, N_B, H)^t$$

As a consequence, $w(Z)$ is a homogenous function of degree 0 of Z .

The dynamics of the system is then given by energy and material balances:

$$\begin{cases} \frac{dN_A}{dt} = F_{AI} - F_A + \nu_A rV \\ \frac{dN_B}{dt} = F_{BI} - F_B + \nu_B rV \\ \frac{dH}{dt} = \dot{Q}_J + F_{AI}h_{AI} + F_{BI}h_{BI} - (F_A h_A + F_B h_B) \end{cases} \quad (23)$$

where (F_{AI}, F_{BI}) and (F_A, F_B) are the inlet flow rate vector and the outlet flow rate vector respectively and (ν_A, ν_B) the stoichiometric vector. (h_{AI}, h_{BI}) and (h_A, h_B) are the inlet molar enthalpy vector and the molar enthalpy vector respectively, and \dot{Q}_J the heat flux coming from the jacket. The sign of each ν_A and ν_B is deduced from the rule (15).

Let us complete the system dynamics representation with the entropy balance. In fact, on one side using the local equilibrium hypothesis (Groot (1962)), (22) can be written:

$$\frac{dS}{dt} = w^t \frac{dZ}{dt} \quad (24)$$

The entropy balance of S can also directly be written from the second law of thermodynamics:

$$\frac{dS}{dt} = \Phi_s + \Sigma_s \text{ and } \Sigma_s \geq 0 \quad (25)$$

where Φ_s , Σ_s are the entropy exchange flow with environment and the irreversible entropy production respectively. The source term Σ_s is always positive from the second law of thermodynamics. From here the entropy balance (25) is identified with (24) to derive Φ_s and Σ_s (see Couenne (2006)):

$$\Phi_s = F_{AI}s_{AI} + F_{BI}s_{BI} - (F_A s_A + F_B s_B) + \frac{\dot{Q}_J}{T_J} \quad (26)$$

and

$$\Sigma_s = \Sigma_s^{\text{mix.}} + \Sigma_s^{\text{ex.}} + \Sigma_s^{\text{reac.}} \geq 0 \quad (27)$$

where

$$\Sigma_s^{\text{mix.}} = \sum_{i=A}^B \frac{F_{iI}}{T} (h_{iI} - T s_{iI} - \mu_i) \geq 0 \quad (28)$$

$$\Sigma_s^{\text{ex.}} = \left(\frac{\dot{Q}_J}{T} - \frac{\dot{Q}_J}{T_J} \right) \geq 0 \quad (29)$$

$$\Sigma_s^{\text{reac.}} = \left(-\nu_A \frac{\mu_A}{T} - \nu_B \frac{\mu_B}{T} \right) rV \geq 0 \quad (30)$$

$\Sigma_s^{\text{mix.}}$, $\Sigma_s^{\text{ex.}}$ and $\Sigma_s^{\text{reac.}}$ are irreversible entropy productions due to mixing, exchange and reaction, respectively. They are also positive from the second law of thermodynamics. Note that $\Sigma_s^{\text{mix.}}$ and $\Sigma_s^{\text{ex.}}$ depend on the control inputs and that $\Sigma_s^{\text{reac.}}$ depends only on the system states.

Finally let us introduce the definition of the total chemical affinity:

$$\mathcal{A} = -\nu_A \frac{\mu_A}{T} - \nu_B \frac{\mu_B}{T} \quad (31)$$

Finally, we can write for the $\Sigma_s^{\text{reac.}}$ in (27) with (31):

$$\Sigma_s^{\text{reac.}} = \mathcal{A} rV \geq 0 \quad (32)$$

Remark 5. The inequality in (32) always holds for any reaction kinetic constant. We can see that the affinity \mathcal{A}

and rV have the same sign for any evolution; if $\mathcal{A} > 0$ (resp. $\mathcal{A} < 0$) then $rV > 0$ (resp. $rV < 0$) and if $\mathcal{A} = 0$ then $rV = 0$. In other words, the reaction always evolves in the direction of decreasing affinity.

4. PRELIMINARY RESULTS

4.1 A general stability criteria for CSTR

Lemma 1 gives a property of the chemical affinity. It generalizes some results obtained in (Favache (2010)).

Lemma 1. The chemical affinity $\mathcal{A}(N_A, N_B, H)$ verifies (33) for the reaction system for any rV :

$$-\nu_A \frac{\partial \mathcal{A}}{\partial N_A} - \nu_B \frac{\partial \mathcal{A}}{\partial N_B} \geq 0 \quad (33)$$

Proof. Let us note that as presented in (22), $w = \left(\frac{-\mu_A}{T}, \frac{-\mu_B}{T}, \frac{1}{T} \right)^t$ is a function of $Z = (N_A, N_B, H)^t$. From (31), we obtain:

$$\frac{\partial \mathcal{A}}{\partial N_i} = - \sum_{j=A}^B \nu_j \frac{\partial \frac{\mu_j}{T}}{\partial N_i}; \quad i = A, B$$

Taking into account that $-\frac{\mu_i}{T} = \frac{\partial S}{\partial N_i}$ (see (22)), we have:

$$\frac{\partial \mathcal{A}}{\partial N_i} = \sum_{j=A}^B \nu_j \frac{\partial^2 S}{\partial N_i \partial N_j}; \quad i = A, B \quad (34)$$

Multiplying (34) by ν_i and summing for $i = A, B$, we obtain

$$\sum_{i=A}^B \nu_i \frac{\partial \mathcal{A}}{\partial N_i} = \sum_{i=A}^B \sum_{j=A}^B \nu_i \nu_j \frac{\partial^2 S}{\partial N_i \partial N_j} \quad (35)$$

(35) can be also written under the following quadratic form (36):

$$\sum_{i=1}^{n_c} \nu_i \frac{\partial \mathcal{A}}{\partial N_i} = \mathbf{v}^t \mathbb{H}(S) \mathbf{v} \quad (36)$$

where $\mathbf{v} = \left(0, \nu_A, \nu_B \right)^t$ and $\mathbb{H}(S)$ is the Hessian matrix of the entropy function $S(Z)$. Because $S = S(Z)$ is concave with respect to $Z = \left(N_A, N_B, H \right)$ (see Remark (10), Callen (1985)): $\mathbb{H}(S) \leq 0$. (33) immediately follows. \square

The following Corollary 1 gives the explicit form of (33) in the ideal mixture.

Corollary 1. Under the hypothesis (H1), the explicit form of (33) is :

$$-\nu_A \frac{\partial \mathcal{A}}{\partial N_A} - \nu_B \frac{\partial \mathcal{A}}{\partial N_B} = \frac{R}{N_t} \mathbf{v}^t \Xi \mathbf{v} + \left(\mathbf{v}^t \mathbf{h} \right)^2 \frac{1}{C_p T^2} \geq 0 \quad (37)$$

where $\mathbf{v} = (\nu_A, \nu_B)^t$, $\mathbf{h} = (h_A, h_B)^t$ and Ξ is the 2×2 positive definite matrix:

$$\Xi = \begin{pmatrix} \frac{N_t - N_A}{N_A} & -1 \\ -1 & \frac{N_t - N_B}{N_B} \end{pmatrix} \quad (38)$$

$C_p = c_{pA} N_A + c_{pB} N_B$ is total heat capacity and $N_t = (N_A + N_B)$ is total molar number.

Proof. See Appendix A. \square

The following proposition 1 proposes a (general) stability criterion for CSTR's. It generalizes some results of the Lemma 1 and the irreversible entropy production.

Proposition 1. For any non isothermal homogeneous liquid-phase reaction in entropy vision, there always exists a thermodynamic potential $P(N_A, N_B, H)$ verifying:

$$\left(-\nu_A \frac{\partial P}{\partial N_A} - \nu_B \frac{\partial P}{\partial N_B} \right) rV \geq 0 \quad (39)$$

(39) is then called the (general) stability criterion.

Proof. We can show that:

- $P = -S$ verifies (39) using the expression of $\Sigma_s^{\text{reac.}}$ given in (27) and relations between the intensive variables and extensive variables in (22).
- $P = \frac{\mathcal{A}^2}{2}$ verifies (39) using (32) and (33). \square

Remark 6. The inequality in (39) always holds for any reaction kinetic constant. We can see that the potential P and rV also have the same sign for any evolution.

5. THERMODYNAMICALLY PORT HAMILTONIAN BASED CSTR MODELING

In this paper, we consider for control purpose and the use of the availability function that the total mass m_t is constant B. As consequence, the outlet molar flow can be expressed directly from mole fractions and inlet flows of the different species involved in the reaction as (see Appendix C):

$$\begin{cases} F_A = \frac{N_A M_A}{m_t} F_{AI} + \frac{N_A M_B}{m_t} F_{BI} \\ F_B = \frac{N_B M_A}{m_t} F_{AI} + \frac{N_B M_B}{m_t} F_{BI} \end{cases} \quad (40)$$

The non isothermal balance equations are given in (23) and are rewritten as in (41) using (40):

$$\frac{dx}{dt} = f + g u \quad (41)$$

with

$$x = \begin{pmatrix} N_A \\ N_B \\ H \end{pmatrix}, \quad u = \begin{pmatrix} F_{AI} \\ F_{BI} \\ \dot{Q}_J \end{pmatrix}, \quad f = \begin{pmatrix} \nu_A rV \\ \nu_B rV \\ 0 \end{pmatrix} \quad (42)$$

$$g = \begin{pmatrix} \left(1 - \frac{N_A M_A}{m_t}\right) & -\frac{N_A M_B}{m_t} & 0 \\ -\frac{N_B M_A}{m_t} & \left(1 - \frac{N_B M_B}{m_t}\right) & 0 \\ \left[h_{AI} - \frac{M_A H}{m_t}\right] & \left[h_{BI} - \frac{M_B H}{m_t}\right] & 1 \end{pmatrix} \quad (43)$$

In our recent results Hoang (2010b), we showed that the internal energy of the system can be chosen as Hamiltonian. The system is then naturally under Hamiltonian form without dissipation, showing that internal energy is conserved. However this formulation does not allow to express the inherent irreversibility of the reaction from the thermodynamic point of view. As a consequence, the

entropy representation must be chosen and the state variables are $Z = (N_A, N_B, H)^t$. In this section we show that the proposed criterion (see Proposition 1) can help to obtain a Port hamiltonian representation with dissipation using the B-M formulation for the system (41). We only treat the non isothermal case in this paper (however, the isothermal case is deduced by the same procedure).

Proposition 2. In the entropy representation, if the thermodynamic potential P given in Proposition 1 verifies the following condition:

$$\lim_{r \rightarrow 0} \frac{\left(\nu_A \frac{\partial P}{\partial N_A} + \nu_B \frac{\partial P}{\partial N_B} \right)}{r} < \infty \quad (44)$$

Then the dynamics (41) accepts a port (pseudo) hamiltonian representation (9) with $x = (N_A, N_B, H)^t$ and:

- Its Hamiltonian is

$$\mathcal{H}(x) = P(x) \quad (45)$$

- Structure matrices are

$$J = \frac{1}{2\Delta} \begin{pmatrix} 0 & J_{12} & -4\alpha b e \left(\frac{\nu_A}{\nu_B} \right)^2 \\ -J_{12} & 0 & ec \\ 4\alpha b e \left(\frac{\nu_A}{\nu_B} \right)^2 & -ec & 0 \end{pmatrix} \quad (46)$$

$$\text{with } J_{12} = \frac{(-4\alpha b \frac{\nu_A}{\nu_B} - 2c)\beta e^2}{4(1-\alpha)b} \text{ and}$$

$$R = -\frac{1}{2\Delta} \begin{pmatrix} R_{11} & \frac{\alpha\beta e^2 \frac{\nu_A}{\nu_B}}{(1-\alpha)} & 4\alpha b e \left(\frac{\nu_A}{\nu_B} \right)^2 \\ \frac{\alpha\beta e^2 \frac{\nu_A}{\nu_B}}{(1-\alpha)} & R_{22} & -ec \\ 4\alpha b e \left(\frac{\nu_A}{\nu_B} \right)^2 & -ec & R_{33} \end{pmatrix} \quad (47)$$

where $0 < \alpha < 1$ and $\beta > 1$ are two scalars

$$\text{and } R_{11} = \frac{2\alpha\beta e^2 \left(\frac{\nu_A}{\nu_B} \right)^2}{(1-\alpha)}, \quad R_{22} = \frac{\beta e^2}{2(1-\alpha)} \text{ and } R_{33} = 2 \left[4\alpha b \left(b \left(\frac{\nu_A}{\nu_B} \right)^2 + c \frac{\nu_A}{\nu_B} \right) + c^2 \right]$$

$$\begin{cases} b = \frac{1}{\nu_A} \left(\frac{\nu_B}{\nu_A} \frac{\partial P}{\partial N_B} + \frac{\partial P}{\partial N_A} \right) \frac{1}{rV} \\ c = -\frac{1}{\nu_A} \frac{\partial P}{\partial N_B} \frac{1}{rV} \\ e = -\frac{1}{\nu_A} \left(\frac{\partial P}{\partial H} \frac{1}{rV} \right) \\ \Delta = \frac{\alpha\beta e^2}{(1-\alpha)} \left(b \left(\frac{\nu_A}{\nu_B} \right)^2 + c \frac{\nu_A}{\nu_B} \right) + \frac{\beta e^2 c^2}{4(1-\alpha)b} \end{cases} \quad (48)$$

- The input-state map is g given by equation(43)
- The control input and the output y are respectively:

$$u^t = (F_{AI} \ F_{BI} \ \dot{Q}_J) \quad (49)$$

and

$$y = g^t \nabla_x \mathcal{H}(x) \quad (50)$$

Finally, the system is passive with dissipation (12),

$$d = \left(\nu_A \frac{\partial P}{\partial N_A} + \nu_B \frac{\partial P}{\partial N_B} \right) rV \quad (51)$$

is negative.

Proof. The proof is done by using the B-M Formulation (see Section 2) and contains two parts.

Part 1: We write the dynamic (41) into B-M formulation. Let us note:

$$Q(x) = \begin{pmatrix} q_{11}(x) & q_{12}(x) & q_{13}(x) \\ q_{21}(x) & q_{22}(x) & q_{23}(x) \\ q_{31}(x) & q_{32}(x) & q_{33}(x) \end{pmatrix} \quad (52)$$

We have from (4),

$$Q(x)f(x) = \nabla_x P(x)$$

where f is given in (41). So the can be established following relations:

$$\begin{aligned} q_{11} &= \frac{1}{\nu_A} \left(-\nu_B q_{12} + \frac{\partial P}{\partial N_A} \frac{1}{rV} \right) \\ q_{21} &= \frac{1}{\nu_A} \left(-\nu_B q_{22} + \frac{\partial P}{\partial N_B} \frac{1}{rV} \right) \\ q_{31} &= \frac{1}{\nu_A} \left(-\nu_B q_{32} + \frac{\partial P}{\partial H} \frac{1}{rV} \right) \end{aligned} \quad (53)$$

Using the condition (39) and after some mathematical manipulations, we obtain (see Appendix D):

$$Q(x) = \begin{pmatrix} b & c & 0 \\ -4\alpha b \frac{\nu_A}{\nu_B} - c & 4\alpha b \left(\frac{\nu_A}{\nu_B} \right)^2 & 0 \\ -e & 0 & \frac{\beta e^2}{4(1-\alpha)b} \end{pmatrix} \quad (54)$$

where $0 < \alpha < 1$ and $\beta > 1$ are two scalars and b, c and e are given in (48).

Part 2: We have from (54):

$$Q(x)^{-1} = \frac{1}{\Delta} \begin{pmatrix} q_{11}^{-1} & \frac{-\beta e^2 c}{4(1-\alpha)b} & 0 \\ \frac{-\left(-4\alpha b \frac{\nu_A}{\nu_B} - c\right)\beta e^2}{4(1-\alpha)b} & q_{22}^{-1} & 0 \\ 4\alpha b e \left(\frac{\nu_A}{\nu_B} \right)^2 & -ec & q_{33}^{-1} \end{pmatrix} \quad (55)$$

with $q_{11}^{-1} = \frac{\alpha \beta e^2 \left(\frac{\nu_A}{\nu_B} \right)^2}{(1-\alpha)}$, $q_{22}^{-1} = \frac{\beta e^2}{4(1-\alpha)}$ and $q_{33}^{-1} = 4\alpha b \left(b \left(\frac{\nu_A}{\nu_B} \right)^2 + c \frac{\nu_A}{\nu_B} \right) + c^2$ with Δ is given as in (48). The dynamics (41) with the matrix $Q(x)$ becomes (7) or it is equivalent to (8). The port hamiltonian representation is then given by (9) with $\mathcal{H}(x) = P(x)$. We obtain for the structure matrices J in (46) and R in (47). Other results (49) and (50) follow immediately. Finally, we calculate for the dissipation term d (12):

$$d = -\left(\nabla_x P(x) \right)^t R \left(\nabla_x P(x) \right) \quad (56)$$

With R given in (47) and from (D.11), $\nabla_x P(x) = \left((\nu_B c + \nu_A b), -\nu_A c, -\nu_A e \right)^t rV$, the quadratic form (56) is:

$$\begin{aligned} d &= \frac{(rV)^2}{2\Delta} \left(\frac{2\alpha\beta e^2 \left(\frac{\nu_A}{\nu_B} \right)^2}{(1-\alpha)} (\nu_B c + \nu_A b)^2 \right. \\ &\quad \left. + \frac{\beta e^2}{2(1-\alpha)} (-\nu_A c)^2 + 2 \frac{\alpha\beta e^2 \frac{\nu_A}{\nu_B}}{(1-\alpha)} (\nu_B c + \nu_A b)(-\nu_A c) \right) \end{aligned} \quad (57)$$

By simplifying (57), we obtain:

$$d = \frac{(rV)^2}{\Delta} \left(\frac{\alpha\beta e^2}{(1-\alpha)} \left(b^2 \left(\frac{\nu_A}{\nu_B} \right)^2 + c b \frac{\nu_A}{\nu_B} \right) \nu_A^2 + \frac{\beta e^2}{4(1-\alpha)} \nu_A^2 c^2 \right) \quad (58)$$

By putting $\nu_A^2 b$ as common factor, (58) becomes:

$$d = \frac{\nu_A^2 b (rV)^2}{\Delta} \left(\frac{\alpha\beta e^2}{(1-\alpha)} \left(b \left(\frac{\nu_A}{\nu_B} \right)^2 + c \frac{\nu_A}{\nu_B} \right) + \frac{\beta e^2}{4(1-\alpha)b} c^2 \right) \quad (59)$$

And with (48) for Δ and b , we obtain d as given in (51). It is negative using (39). \square

Remark 7. The dissipation d (51) don't depend on α and β .

Remark 8. In the non-equilibrated reaction, the condition (44) verifies because $r > 0$. In the equilibrated reaction we can show that the condition (44) also verifies using the fact that:

- The chemical affinity (31) can be rewritten under a structured form:

$$\mathcal{A} = \mathcal{A}_f - \mathcal{A}_r \quad (60)$$

where $\mathcal{A}_f = -\nu_A \frac{\mu_A}{T}$ and $\mathcal{A}_r = \nu_B \frac{\mu_B}{T}$ are affinities of the forward and reserve reactions respectively.

- The global reaction rate is then given by (Tarbell (1977); Couenne (2006))

$$r = k(T) \left(\exp \left(\frac{\mathcal{A}_f}{R} \right) - \exp \left(\frac{\mathcal{A}_r}{R} \right) \right) \quad (61)$$

where $k(T) > 0$ is the kinetic constant and R is the gas constant. (60) and (61) always permit to verify the inequality (32).

- Finally, we can show that,

$$\lim_{r \rightarrow 0} \frac{\mathcal{A}}{r} < \infty$$

Remark 9. The obtained results give a global dissipative behavior for non isothermal case without doing any variable transformation as done in Otero-Muras (2008). More precisely, the authors in Otero-Muras (2008) used the affinity as hamiltonian storage function and gave a local hamiltonian representation of the isolated chemical systems (see the proposition 1 and the equ. (34) in Otero-Muras (2008)). In fact, the equ. (34) in Otero-Muras (2008) close to equilibrium becomes (using Taylor series) $\mathcal{H}(z) = C \frac{z^2}{2}$ with $C = cst$ and z is the affinity \mathcal{A} .

6. CONCLUSION

In this paper we have developed a thermodynamic stability criteria for CSTRs. Furthermore in the non isothermal case, we have then proposed links between the Brayton-Moser formulation and Port (pseudo) Hamiltonian modeling of CSTR with one liquid-phase reaction $\nu_A A = \nu_B B$. The very interesting result is that a solution of the Brayton-Moser formulation is easily found using the developed criteria. As a consequence, the dissipation term of the hamiltonian modeling captures the natural irreversibility due to chemical reaction.

REFERENCES

- Brogliato, B. and Lozano, R. and Maschke, B. and Egeland, O. (2007). *Dissipative systems analysis and control*. Springer, London, 2nd edition.
- van der Schaft, A. (2000a). Port-controlled Hamiltonian systems: towards a theory for control and design of nonlinear physical systems. *SICE journal*, 39(2), 91-98.
- van der Schaft, A. (2000b). *L₂-gain and passivity techniques in nonlinear control*. Springer-Verlag, London, 2nd ed.
- Maschke, B. and Ortega, R. and Arjan J. van der Schaft (2000). Energy based Lyapunov functions for forced Hamiltonian systems with dissipation. *IEEE Trans. on Autom. Control*, 45(8), 1498-1502.
- Eberard, D. and Maschke, B. and van der Schaft, A. (2007). An extension of pseudo-Hamiltonian systems to the thermodynamic space: towards a geometry of non-equilibrium thermodynamics. *Reports on Mathematical Physics*, 60(2), 175-198.
- Hangos, K. M. and Bokor, J. and Szederkényi, G. (2001). Hamiltonian view on process systems, *AIChE journal*, vol. 47, no 8, pp. 1819-1831.
- Otero-Muras, I. and Szederkényi, G. and Alonso, A. A. and Hangos, K. M. (2008). Local dissipative Hamiltonian description of reversible reaction networks. *Systems & Control Letters*, 57(7):554-560.
- Dörfler F. and Johnsen J.K. and Allgöwer F. (2009). An introduction to interconnection and damping assignment passivity-based control in process engineering. *Journal of Process Control*, 19, 1413-1426.
- Favache, A. and Dochain, D. (2009). Power-shaping control of an exothermic continuous stirred tank reactor (CSTR). In *proceedings of IFAC-ADCHEM*, Turkey. 101-110.
- Favache, A. and Dochain, D. (2010). Towards power-shaping control of the CSTR: from thermodynamics to the Brayton-Moser formulation of the dynamics. In *proceedings of IFAC-DYCOPS*, Leuven, Belgium. 701-706
- Ramírez, H. and Sbarbaro, D. and Ortega, R. (2009). On the control of non-linear processes: An IDA-PBC approach. *Journal of Process Control*, 19, 405-414.
- Hoang, H. and Couenne, F. and Jallut, C. and Le Gorrec, Y. (2008). Lyapunov based control for non isothermal continuous stirred tank reactor. *IFAC World congress*, Korea. 3854-3858.
- Hoang, H. and Couenne, F. and Jallut, C. and Le Gorrec, Y. (2009). Thermodynamic approach for Lyapunov based control. In *proceedings of IFAC-ADCHEM*, Turkey. 367-372.
- Hoang, H. and Couenne, F. and Jallut, C. and Le Gorrec, Y. (2010a). Hamiltonian formulation and IDA-PBC control of non isothermal continuous stirred tank reactors. In *proceedings of IFAC-DYCOPS*, Leuven, Belgium.
- Hoang, H. and Couenne, F. and Jallut, C. and Le Gorrec, Y. (2010b). Port Hamiltonian based modeling and control of exothermic Continuous Stirred Tank Reactors. In *proceedings of IFAC-NOLCOS*, Bologna, Italia.
- Ortega, R. and van der Schaft, A. and Maschke, B. and Escobar, G. (2002). Interconnection and damping assignment passivity-based control of port-controlled Hamiltonian Systems. *Automatica*, 38, 585-596.
- Brayton, R. K and Moser J. K. (1964). A theory of nonlinear networks I., *Quarterly of applied mathematics*, 22:1-33.
- Couenne, F. and Jallut, C. and Maschke, B. and Breedveld, P. C. and Tayakout, M. (2006). Bond graph modelling for chemical reactors. *Mathematical and Computer Modelling of Dynamical Systems*, 12(2-3), 159-174.
- Alonso, A.A. and Ydstie, B.E. (1996). Process systems, passivity and the second law of thermodynamics, *Computers and Chemical Engineering*, 20(2):1119-1124.
- Ydstie, B.E., and Alonso, A.A. (1997). Process systems and passivity via the Clausius-Planck inequality. *Systems Control Letters*, 30(5), 253-264.
- Alonso, A.A. and Ydstie, B.E. (2001). Stabilization of Distributed Systems using Irreversible Thermodynamics, *Automatica*, 37 :1739-1755.
- Ruszkowski, M., Garcia-Osorio, V., and Ydstie, B.E. (2005). Passivity based control of transport reaction systems. *AIChE Journal*, 51, 3147-3166.
- Jillson, K.R. and Ydstie B.E. (2007). Process networks with decentralized inventory and flow control. *Journal of Process Control*, 17, 399-413.
- Sandler, S. I. (1999). *Chemical and Engineering Thermodynamics*. Wiley and Sons, 3rd edition.
- Groot, S. R. de and Mazur, P. (1962) *Non-equilibrium thermodynamics*. Dover Pub. Inc., Amsterdam, 1st ed.
- Glansdorff, P. and Prigogine, I. (1971). *Thermodynamic theory of structure, stability and fluctuations*. Wiley-Interscience.
- Callen, H.B. (1985). *Thermodynamics and an introduction to thermostatics*. John Wiley & Sons, New York, 2nd ed.
- Tarbell, J. M. (1977). A thermodynamic Lyapunov function for the near equilibrium CSTR. *Chemical Engineering Science*, 32:1471-1476.
- Jie Bao and Peter L. Lee (2007). *Process control: the passive systems approach*. Springer.
- Hudon, N. and Hoffner, K. and Guay, M. (2008). Equivalence to dissipative Hamiltonian realization. In *proceedings of 47th IEEE Conference on Decision and Control*. 3163-3168.

Appendix A. PROOF FOR COROLLARY 1

The isobaric mixture is ideal, we have for the partial molar enthalpies and entropies of the chemical specie k (Sandler (1999)):

$$\begin{cases} h_k(T, x_k) = c_{pk}(T - T_{ref}) + h_{kref} \\ s_k(T, x_k) = c_{pk} \ln \left(\frac{T}{T_{ref}} \right) + s_{kref} - R \ln x_k \end{cases} \quad (\text{A.1})$$

where x_k is molar fraction of species $k = A, B$:

$$x_k = \left(\frac{N_k}{N_A + N_B} \right) \quad (\text{A.2})$$

And the fact that $\frac{\mu_k}{T} = \frac{h_k}{T} - s_k$ (Groot (1962); Sandler (1999)), we obtain:

$$\left[\frac{\mu_k}{T} \right] (T, x_k) = \xi_k(T) + R \ln x_k \quad (\text{A.3})$$

with

$$\xi_k(T) = c_{pk} + \frac{-c_{pk}T_{ref} + h_{kref}}{T} - c_{pk} \ln\left(\frac{T}{T_{ref}}\right) - s_{kref} \quad (\text{A.4})$$

The intensive variables (A.3) is not presented with respect to its true variables $Z = (N_A, N_B, H)$. Let us do a variable transformation as bellow; because the mixture is ideal we can write for the total enthalpy:

$$H(T, N_k) = \sum_{k=A}^B h_k N_k \quad (\text{A.5})$$

Using the first relation in (A.1), (A.5) leads to

$$T(H, N_A, N_B) = \frac{H - \sum_{k=A}^B N_k h_{kref}}{\sum_{k=A}^B N_k c_{pk}} + T_{ref} \quad (\text{A.6})$$

From here $\left[\frac{\mu_k}{T}\right](T, x_k)$ in (A.3) with (A.6) and (A.2) becomes $\left[\frac{\mu_k}{T}\right](H, N_A, N_B)$. We obtain for \mathcal{A} (31):

$$\nu_i \frac{\partial \mathcal{A}}{\partial N_i} = -\nu_i \nu_A \frac{\partial \frac{\mu_A}{T}}{\partial N_i} - \nu_i \nu_B \frac{\partial \frac{\mu_B}{T}}{\partial N_i} = -\nu_i \sum_{j=A}^B \nu_j \frac{\partial \frac{\mu_j}{T}}{\partial N_i} \quad (\text{A.7})$$

Using (A.3) and (A.6), it leads to

$$\begin{aligned} \nu_i \frac{\partial \mathcal{A}}{\partial N_i} &= -\nu_i \sum_{j=A}^B \nu_j \frac{\partial \xi_j(T)}{\partial T} \frac{\partial T}{\partial N_i} \\ &\quad - \nu_i R \sum_{j=A}^B \nu_j \frac{\partial \left(\ln \left(\frac{N_j}{N_A + N_B} \right) \right)}{\partial N_i} \end{aligned} \quad (\text{A.8})$$

Let us note that from (A.4) $\frac{\partial \xi_k(T)}{\partial T} = -\frac{h_k}{T^2}$, (A.6) $\frac{\partial T}{\partial N_i} = -\frac{h_i}{C_p}$ and that:

$$\frac{\partial \left(\ln \left(\frac{N_j}{N_A + N_B} \right) \right)}{\partial N_i} = \begin{cases} \frac{N_t - N_i}{N_i N_t} & \text{if } i = j \\ -\frac{1}{N_t} & \text{if } i \neq j \end{cases}$$

We obtain for (A.7):

$$\begin{aligned} \nu_i \frac{\partial \mathcal{A}}{\partial N_i} &= -\left(\nu_A \frac{h_A}{T^2} + \nu_B \frac{h_B}{T^2} \right) \nu_i \frac{h_i}{C_p} \\ &\quad - R \nu_i \left(-\frac{1}{N_t} \sum_{j=A, j \neq i}^B \nu_j + \nu_i \frac{N_t - N_i}{N_i N_t} \right) \end{aligned} \quad (\text{A.9})$$

Get sum for (A.9) with $i = A, B$ one obtains:

$$\begin{aligned} -\sum_{i=A}^B \nu_i \frac{\partial \mathcal{A}}{\partial N_i} &= \frac{1}{T^2 C_p} \left(\nu_A h_A + \nu_B h_B \right)^2 \\ &\quad + \frac{R}{N_t} \sum_{i=A}^B \nu_i \left(-\sum_{j=A, j \neq i}^B \nu_j + \nu_i \frac{N_t - N_i}{N_i} \right) \end{aligned} \quad (\text{A.10})$$

The eq. (A.10) leads to (37). The later ends the proof.

Appendix B. THERMODYNAMIC AVAILABILITY.

As a consequence of the second law of thermodynamics for homogeneous systems, the entropy function $S(Z)$ is necessarily concave with respect to Z (see Callen (1985)).

This concavity is independent from the dynamic behavior of the system. From the concavity of $S(Z)$, it can be shown (see (Glansdorff and Prigogine (1971); Alonso and Ydstie (1996); Ydstie and Alonso (1997))) that the *the availability function* \mathcal{A} :

$$\mathcal{A}(Z) = S_2 + w_2^t(Z - Z_2) - S(Z) \geq 0 \quad (\text{B.1})$$

is non negative, where Z_2 is some fixed reference point (for example the desired set point for control) and w_2 is intensive variables associated to the extensive variables Z_2 . $\mathcal{A}(Z)$ has some interesting properties that will entail its use as Lyapunov function for control purpose (Alonso and Ydstie (2001); Ruszkowski (2005); Hoang (2008, 2009, 2010a,b)).

Remark 10. Because the entropy S is an homogeneous function of degree 1 with respect to Z (Callen (1985)), it is not strictly concave in general case, as a consequence $\mathcal{A}(Z)$ will not be strictly convex. The strict concavity of the entropy can be obtained if at least one global extensive property (such volume, total mass, total mole number) is fixed (Jillson (2007)). In the remaining of the paper we will always suppose that the total mass m_t is constant.

Finally, the availability function (B.1) can be written (see (Hoang (2010b))):

$$\mathcal{A}(Z) = -(w - w_2)^t Z \quad (\text{B.2})$$

and

$$\frac{d\mathcal{A}}{dt} = -(w - w_2)^t \frac{dZ}{dt} \quad (\text{B.3})$$

Appendix C. OUTLET MOLAR FLOWS

The total mass is constant:

$$m_t = M_A N_A + M_B N_B = cte \quad (\text{C.1})$$

where M_A and M_B are molar masses of species A and B .

As a matter of fact, the considered constraint allows to express the outlet molar flows as function of inlet molar flows and mole numbers. In fact, from this constraint we get:

$$\frac{dm_t}{dt} = M_A \frac{dN_A}{dt} + M_B \frac{dN_B}{dt} = 0 \quad (\text{C.2})$$

From stoichiometric relation $(M_A \nu_A + M_B \nu_B) rV = 0$, so we obtain f:

$$(M_A F_{AI} + M_B F_{BI}) - (M_A F_A + M_B F_B) = 0 \quad (\text{C.3})$$

On one side, F_A and F_B can be expressed with respect to the total molar flow rate F_t as:

$$\begin{pmatrix} F_A \\ F_B \end{pmatrix} = \begin{pmatrix} \frac{N_A}{N_t} \\ \frac{N_B}{N_t} \end{pmatrix} F_t \quad (\text{C.4})$$

where N_t is the total molar number. We obtain from (C.4) with (C.1):

$$M_A F_A + M_B F_B = \frac{m_t}{N_t} F_t \quad (\text{C.5})$$

So (C.4) can be written as:

$$\begin{pmatrix} F_A \\ F_B \end{pmatrix} = \begin{pmatrix} \frac{N_A M_A}{m_t} & \frac{N_A M_B}{m_t} \\ \frac{N_B M_A}{m_t} & \frac{N_B M_B}{m_t} \end{pmatrix} \begin{pmatrix} F_{AI} \\ F_{BI} \end{pmatrix} \quad (\text{C.6})$$

This equation (C.6) leads to (40).

Appendix D. PROOF FOR PROPOSITION 1

We choose $q_{13} = q_{23} = q_{32} = 0$, (52) becomes:

$$Q = \begin{pmatrix} \frac{1}{\nu_A} \chi_A & q_{12} & 0 \\ \frac{1}{\nu_A} \chi_B & q_{22} & 0 \\ \chi_H & 0 & q_{33} \end{pmatrix} \quad (D.1)$$

with $\chi_A = -\nu_B q_{12} + \frac{\partial P}{\partial N_A} \frac{1}{rV}$, $\chi_B = -\nu_B q_{22} + \frac{\partial P}{\partial N_B} \frac{1}{rV}$ and $\chi_H = \frac{1}{\nu_A} \frac{\partial P}{\partial H} \frac{1}{rV}$. This matrix $Q + Q^t$ is (strictly) negative definite if and only if

$$-(Q + Q^t) > 0$$

As a consequence, all of the principal minors determinants of $-(Q + Q^t)$ are positive. We obtain the following conditions:

$$\begin{cases} 2 \frac{1}{\nu_A} \chi_A < 0 \\ 4q_{22} \frac{1}{\nu_A} \chi_A - \left(q_{12} + \frac{1}{\nu_A} \chi_B\right)^2 > 0 \\ 2q_{33} \left\{ 4 \frac{1}{\nu_A} \chi_A q_{22} - \left(q_{12} + \frac{1}{\nu_A} \chi_B\right)^2 \right\} - 2q_{22} \chi_H^2 < 0 \end{cases} \quad (D.2)$$

Calculation for q_{12} . The property (39) helps us to choose in this non isothermal case:

$$q_{12} = -\frac{1}{\nu_A} \frac{\partial P}{\partial N_B} \frac{1}{rV} \quad (D.3)$$

So the first relation of (D.2) always verifies because:

$$2 \frac{1}{\nu_A} \left(-\nu_B q_{12} + \frac{\partial P}{\partial N_A} \frac{1}{rV} \right) = 2 \frac{1}{\nu_A^2} \left(\nu_B \frac{\partial P}{\partial N_B} + \nu_A \frac{\partial P}{\partial N_A} \right) \frac{1}{rV}$$

is certainly negative with (39).

Calculation for q_{22} . The second relation of (D.2) becomes:

$$q_{22} \left(4 \frac{1}{\nu_A} \chi_A - \left(\frac{\nu_B}{\nu_A} \right)^2 q_{22} \right) > 0 \quad (D.4)$$

Because $\frac{1}{\nu_A} \chi_A < 0$ (see (D.2)) and the equation (D.4) is the second order with respect to q_{22} . (D.4) is positive if we have:

$$0 > q_{22} > \left(\frac{\nu_A}{\nu_B} \right)^2 4 \frac{1}{\nu_A} \left(-\nu_B q_{12} + \frac{\partial P}{\partial N_A} \frac{1}{rV} \right) \quad (D.5)$$

From (D.5), we can choose for q_{22} by using q_{12} in (D.3):

$$q_{22} = \left(\frac{\nu_A}{\nu_B} \right)^2 \left(4\alpha \frac{1}{\nu_A} \left(\frac{\nu_B}{\nu_A} \frac{\partial P}{\partial N_B} + \frac{\partial P}{\partial N_A} \right) \frac{1}{rV} \right) < 0 \quad (D.6)$$

with $0 < \alpha < 1$.

Calculation for q_{33} . The third condition of (D.2) permits to determine q_{33} . In fact, we have:

$$2q_{33} \left\{ 4 \frac{1}{\nu_A} \left(\frac{\nu_B}{\nu_A} \frac{\partial P}{\partial N_B} + \frac{\partial P}{\partial N_A} \right) \frac{1}{rV} q_{22} - \left(\frac{\nu_B}{\nu_A} \right)^2 q_{22}^2 \right\} - 2q_{22} \chi_H^2 < 0 \quad (D.7)$$

By using relation (D.6) for q_{22} , it leads to $\frac{1}{\alpha} q_{22} \left(\frac{\nu_B}{\nu_A} \right)^2 = \frac{4}{\nu_A} \left(\frac{\nu_B}{\nu_A} \frac{\partial P}{\partial N_B} + \frac{\partial P}{\partial N_A} \right) \frac{1}{rV}$. The condition (D.7) then becomes:

$$2q_{22} \left\{ q_{33} \left(\frac{1-\alpha}{\alpha} \right) \left(\frac{\nu_B}{\nu_A} \right)^2 q_{22} - \chi_H^2 \right\} < 0 \quad (D.8)$$

We notice that $q_{22} < 0$ and the equation (D.8) is linear with respect to q_{33} . (D.8) is negative only if the condition for q_{33} is:

$$q_{33} < \frac{\left(\frac{1}{\nu_A} \frac{\partial P}{\partial H} \frac{1}{rV} \right)^2}{\left(\frac{1-\alpha}{\alpha} \right) \left(\frac{\nu_B}{\nu_A} \right)^2 q_{22}} < 0 \quad (D.9)$$

q_{33} is also negative because the negation of q_{22} (D.6). We choose:

$$q_{33} = \frac{\beta \left(\frac{1}{\nu_A} \frac{\partial P}{\partial H} \frac{1}{rV} \right)^2}{4(1-\alpha) \frac{1}{\nu_A} \left(\frac{\nu_B}{\nu_A} \frac{\partial P}{\partial N_B} + \frac{\partial P}{\partial N_A} \right) \frac{1}{rV}} < 0 \quad (D.10)$$

with $\beta > 1$. In order to simplify some used notations, we note:

$$\begin{cases} \frac{\partial P}{\partial N_A} = (\nu_B c + \nu_A b)(rV) \\ \frac{\partial P}{\partial N_B} = -\nu_A c(rV) \\ \frac{\partial P}{\partial H} = -\nu_A e(rV) \end{cases} \Rightarrow \begin{cases} b = \frac{1}{\nu_A} \left(\frac{\nu_B}{\nu_A} \frac{\partial P}{\partial N_B} + \frac{\partial P}{\partial N_A} \right) \frac{1}{rV} \\ c = -\frac{1}{\nu_A} \frac{\partial P}{\partial N_B} \frac{1}{rV} \\ e = -\frac{1}{\nu_A} \left(\frac{\partial P}{\partial H} \frac{1}{rV} \right) \end{cases} \quad (D.11)$$

This equation (D.11) leads to some relations obtained for b , c and e given in (48). The matrix Q (D.1) with (D.3), (D.10) and (D.11) becomes:

$$Q = \begin{pmatrix} b & c & 0 \\ -4\alpha b \frac{\nu_A}{\nu_B} - c & 4\alpha b \left(\frac{\nu_A}{\nu_B} \right)^2 & 0 \\ -e & 0 & \frac{\beta e^2}{4(1-\alpha)b} \end{pmatrix} \quad (D.12)$$

The matrix Q (D.12) is a solution for the B-M formulation (3) of the non isothermal system (41) with $0 < \alpha < 1$ et $\beta > 1$.